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Preconcentration of gold ions from water samples by modified organo-nanoclay sorbent prior to flame atomic absorption spectrometry determination

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This paper is dedicated to the memory of the founder of Kerman University, Mr. Alireza Afzalipour, on the occasion of the centenary of his birth.

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Nanoclay
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Gold determination
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ABSTRACT

In this work, the applicability of modified organo nanoclay as a new and easy prepared solid sorbent for the preconcentration of trace amounts of Au(III) ion from water samples is studied. The organo nanoclay was modified with 5-(4′-dimethylamino benzyliden)-rhodanine and used as a sorbent for separation of Au(III) ions. The sorption of gold ions was quantitative in the pH range of 2.0–6.0. Quantitative desorption occurred with 6.0 mL of 1.0 mol L^{-1} $Na_2S_2O_3$. The amount of eluted Au(III) was measured using flame atomic absorption spectrometry. In the initial solution the linear dynamic range was in the range of 0.45 ng mL^{-1} to 10.0 μg mL^{-1}, the detection limit was 0.1 ng mL^{-1} and the preconcentration factor was 105. Also, the relative standard deviation was ±2.3% ($n = 8$ and $C = 2.0$ μg mL^{-1}) and the maximum capacity of the sorbent was 3.9 mg of Au(III) per gram of modified organo nanoclay. The influences of the experimental parameters including sample pH, eluent volume and eluent type, sample volume, and interference of some ions on the recoveries of the gold ion were investigated. The proposed method was applied for preconcentration and determination of gold in different samples.

1. Introduction

In recent years, great attention has been paid to the application of nano-structure materials. Since clay and clay minerals have primary particles with at least one dimension in the nanometer scale, they may be regarded as nanomaterials of geological and pedological origins [1]. Clay minerals are characterized by certain properties, such as a layer structure with one dimension in the nanometer range, where the thickness of the 1:1 layer is about 0.7 nm, and that of the 2:1 layer is about 1 nm [2] and can react with different types of organic compounds in several ways. Normally, organic surfactants are used to make the surface of clay platelets organophilic and swell the clay galleries. An organophilic surface and interlayer environment can be produced by replacing naturally occurring inorganic exchangeable cations with a variety of organic cations such as long chain alkylammonium ions [3]. These modified organoclays are used in a wide range of applications, such as adsorbents for organic pollutants [4] and metal ions, reinforcing filler plastics and catalysts [5]. Because of their small particle size, the specific surface area (external and internal) of clays and clay minerals extends to a few hundred m^2/g. The nano-size dimension, extensive surface area, and peculiar charge characteristics of nanoclay materials lie behind their large propensity for taking up ions and organic compounds [6]. Therefore, nanoclay may be suitable for preconcentration in solid phase extraction.

Despite the selectivity and sensitivity of analytical techniques such as atomic absorption spectrometry, there is a crucial need for the preconcentration of trace elements before analysis due to their frequent low concentrations in many samples. Additionally, because high levels of other components usually accompany analytes, a clean-up step is often required. Liquid–liquid extraction (LLE) is a classical method for preconcentrating metal ions and matrix removal. Solid phase extraction (SPE) is another approach that offers a number of important benefits [7]. It reduces solvent usage and exposure, disposal costs, and extraction time for sample preparation. Consequently, in recent years SPE has been used successfully for the separation and preconcentration of metal ions in different samples [8].

It is well known that, due to its significant role in biology, environment and industry, gold is one of the most interesting micro amount elements. Even though it can be used as a drug in the supervised therapy of arthritis [9] and cancer [10] in the form of

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different Au(I) and Au(III) compounds, or in radiotherapy of cancer in the form of radioactive isotope ^{198}Au, it may be also very toxic for human and animal organism and plants and accounts as a pollutant, because of its inhibiting effect upon the activity of many enzymes and its preventing effect upon DNA separation [11]. Moreover, gold as a noble metal is one of the most potent sensitizers with a high incidence of allergic reactions like contact dermatitis, rhinitis, conjuctivitis, asthma and utricaria. Gold belongs to the group of elements that occur on the earth in very low natural content. The concentration of Au in natural water is extremely low and its concentration is about 4 ng g^{-1} in basic rocks and 1 ng g^{-1} in soils [12]. The concentration of gold in environmental, geological and metallurgical materials is usually too low to be determined directly by atomic absorption spectroscopy owing to insufficient sensitivity and matrix interferences. Hence, separation and enrichment of analyte are important aspects in determination of gold [13]. Various techniques such as LLE, coprecipitation, SPE, cloud point extraction and electrodeposition [14] have been used for separation and preconcentration of gold. Different sorbents such as Carbon nanotubes [15], Thiol Cotton Fiber [16], Octadecyl Silica Membrane Disks [17], Aminopropyl Silica Gel [18], Silica Gel/NanoMeter TiO_2 [19], Amberlite XAD-2000 resin [20] and Dowex 4195 resin [21] have been used as a sorbent for preconcentration gold ions.

In our previous work, we used the PAN immobilized organo nanoclay as a sorbent for the separation and preconcentration of trace amounts of copper, nickel and manganese ions [22] in water samples. The goal of this study is to explore the performances of modified organo nanoclay as a new sorbent for the preconcentration of gold ions from water samples. Modification of organo nanoclay was performed by 5-(4′-dimethylamino benzyliden)-rhodanine because it can be complexed with gold ions [23]. The applicability of the proposed method for the analysis of different samples is described.

2. Experimental

2.1. Reagents and materials

High purity reagents from Sigma (St. Louis, MO, USA) and Merck (Darmstadt, Germany) were used for all preparations of the standard and sample solutions. A stock solution of diverse elements was prepared from high purity compounds. Gold stock solution of 1000.0 μg mL^{-1} was prepared by dissolving 0.2041 g of $HAuCl_4{\cdot}3H_2O$ (Merck) into a 100.0 mL volumetric flask and diluting to the mark with distilled water. A 0.01% solution of 5-(4′-dimethylamino benzyliden)-rhodanine (Merck) was prepared by dissolving it in ethanol. The nanoclay material is organically modified montmorillonite in a platelet form called Nanomer I30E (Nanocor, USA) with the characteristics of 10 μm long, 1 μm wide, 50 nm thick and 600 m^2 g^{-1} surface area.

2.2. Apparatus

A Varian Model SpectrAA 220 atomic absorption spectrometer was used for determination of gold using an air–acetylene flame. The operating conditions were as follows: wavelength 242.8 nm, lamp current 4.0 mA and slit width 1.0 nm. The acetylene flow and the air flow were 1.0 and 3.5 L min^{-1}, respectively. The pH measurement was carried out using a Metrohm pH meter (model 713) with a combined pH glass electrode calibrated against two standard buffer solutions at pH 4.0 and 7.0. All glassware and columns were washed with a mixture of concentrated HCl and concentrated HNO_3 (1:1) before application.

2.3. Preparation of modified organo nanoclay

Industrial purified commercial organo nanoclay was heated to 50 °C. The treatment was carried out by the dispersion of 25 mL 0.01% (w/v) solution of 5-(4′-dimethylamino benzyliden)-rhodanine reagent in ethanol to 5.0 g of organo nanoclay at room temperature, followed by vigorous stirring for 8 h for adsorption 5-(4′-dimethylamino benzyliden)-rhodanine onto nanoclay. The sample was filtered, washed, and dried at 60 °C and stored until use.

2.4. Determination of gold in water samples

To demonstrate the applicability and reliability of the proposed method for environmental use, the method was applied in the determination of gold in different sample waters including tap water (Mahan drinking water), river water (Gishigan, Rayen), well water (Mahan), sea water (Caspian) and wastewater (Copper factory, Sarcheshmeh). A 300 mL of water sample was adjusted to pH 0.5 with nitric acid immediately after collection, in order to prevent adsorption of the gold ions on the flask walls and filtered to remove any suspended particles. For preconcentration, the pH of the samples was adjusted to 2.5 with a buffer solution before analysing by the described procedure. In addition, the recovery experiments of different amounts of gold were carried out.

2.5. Analysis of gold in certified reference materials

The accuracy and applicability of the proposed method were applied to the determination of gold in Canadian Certified Reference Materials Project (CCRMP) (MA-1b). A 300.0 mg sample was taken in a mixture of HNO_3, HCl and HF (2:4:1 volume ratio), then heated and the solution was left to evaporate thoroughly. Five mL of 0.1 mol L^{-1} HCl was then added and the obtained solution was again warmed for an appropriate time and finally cooled to room temperature, diluted and filtered. The volume of the filtrate was raised to 50.0 mL with de-ionized distilled water in a volumetric flask. An aliquot of the obtained sample solution was taken individually. The content of gold ions was determined after adding buffer solution with pH 2.5.

2.6. Preconcentration procedure

An aliquot of gold solution was taken into a 100 mL beaker. Then, 5 mL of phosphoric acid/potassium dihydrogen phosphate buffer solution with pH ~2.5 was added to it, followed by dilution to ~50 mL with distilled water. 500 mg of modified nanoclay was then added to the solution with continuous stirring for 8 min. The solid mass was separated by filtration on Whatman filter paper (No. 1041). Finally, the separated solid was washed with distilled water and the adsorbed Au(III) ions were eluted with 6.0 mL of 1.0 mol L^{-1} $Na_2S_2O_3$. For eluting the residue was mixed with 6.0 mL of 1.0 mol L^{-1} $Na_2S_2O_3$ and the mixture was shaken vigorously for 5 min and again, the solid mass was separated by filtration on Whatman filter paper and the eluent solution containing Au(III) ion was aspirated directly into the flame atomic absorption spectrometry (FAAS) against the blank prepared in the same manner without addition of Au(III) ions.

3. Results and discussion

Preliminary experiments showed that although Nanomer I30E organo nanoclay has a low tendency for retention of Au(III) adsorption (less than 20%), it is not selective for separation of gold. Therefore, the Nanomer I30E nanoclay is not considered as a suitable sorbent for the separation of gold ions. However, recent work

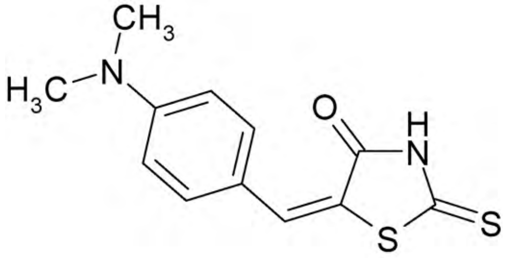

Fig. 1. Structure of 5-(4′-dimethylamino benzyliden)-rhodanine reagent.

[24] indicates that nanoclay can adsorb organic materials. So, the 5-(4′-dimethylamino benzyliden)-rhodanine ligand (Fig. 1) was added to organo nanoclay because it can be complexed with gold ion [23], the modified organo nanoclay was then studied for separation and preconcentration of Au(III) ion. The results showed that the recovery of Au(III) ion by using modified Nanomer I30E nanoclay is higher than 96%. Moreover, modified Nanomer I30E nanoclay is selective for the separation of Au(III) ions. In order to obtain highly sensitive, accurate, and reproducible results, analytical parameters including pH, type and volume of eluent solution and breakthrough volume were optimized for preconcentration of Au(III) ions.

3.1. *Effect of the sample pH*

As pH is one of the important factors affecting the efficiency of retention/elution metal ions by solid phase extraction, the influences of pH of the aqueous solution on the sorption of gold onto the modified nanoclay sorbent were investigated. Adsorption studies were carried out at different pH, keeping the other variables constant. The percent sorption of Au(III) ion on the sorbent surface as a function of the pH of the sample solution was evaluated. It can be seen from Fig. 2 that the maximum sorption of gold on the modified nanoclay sorbent was obtained in the pH range of 2.0–6.0. The pH was therefore maintained at approximately 2.5 in subsequent studies.

3.2. *Evaluation of sorbent property*

The sorption capacity is an important factor because it determines how much sorbent is required for quantitative enrichment of the analyte from a given solution. The sorption capacity of modified nanoclay was determined using 1.0 g of modified organo nanoclay and different volumes of 1000.0 μg mL^{-1} Au(III) added to it. The concentration of Au(III) was determined in effluent solution. When the effluent solution showed high amount of gold, the experiment was stopped and quantity of gold in the concentrate was determined, followed by the determination of retained Au(III) using FAAS. The results showed that the concentration of gold ion in effluent solution was increased after passing 3.9 mL of 1000.0 μg mL^{-1} Au(III). Therefore the maximum capacity of the sorbent was 3.9 mg of Au(III) per gram of sorbent. The modified nanoclay sorbent was subjected to several loadings with the sample solution and subsequent elution. It was found that adsorption properties of the adsorbent remained constant after 15 cycles of sorption and desorption.

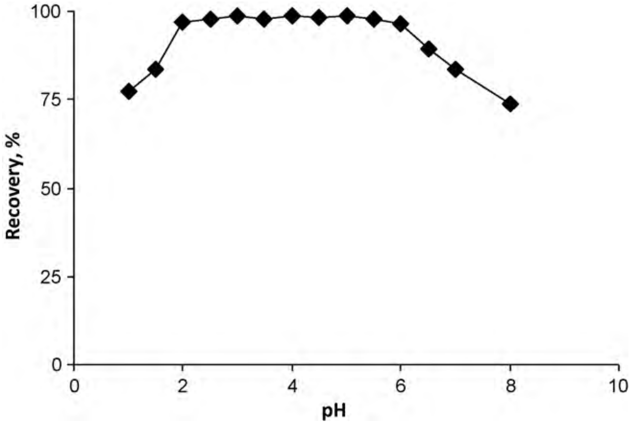

Fig. 2. Effect of the sample solution pH on the percent recovery of Au^{3+} ion. Conditions: Au, 10.0 μg, eluent solution, 6.0 mL of 1.0 mol L^{-1} $Na_2S_2O_3$; instrumental settings: wavelength, 242.8 nm; lamp current, 4.0 mA; slit width, 1.0 nm; acetylene flow, 1.5 L min^{-1}; air flow, 3.5 L min^{-1}.

Table 1
Effect of eluent type on the recovery of gold ion.

Eluent (6.0 mL)	Recovery (%)
Hydrochloric acid (1.0 mol L^{-1})	24.7
Thiourea 3% in hydrochloric acid (1.0 mol L^{-1})	48.5
Thiourea 3% in hydrochloric acid (2.0 mol L^{-1})	50.2
Nitric acid (1.0 mol L^{-1})	17.8
Nitric acid (2.0 mol L^{-1})	21.6
Sodium thiosulfate (0.1 mol L^{-1})	75.1
Sodium thiosulfate (0.2 mol L^{-1})	86.7
Sodium thiosulfate (0.5 mol L^{-1})	93.4
Sodium thiosulfate (0.7 mol L^{-1})	97.3
Sodium thiosulfate (1.0 mol L^{-1})	98.2
Sodium thiosulfate (1.5 mol L^{-1})	98.9

Conditions and instrumental settings were same as in Fig. 2, except eluent type.

3.3. *Selection of eluent*

Other important factors affecting the preconcentration procedure are the type, volume and concentration of the eluent used for the removal of metal ions from the sorbent [7]. A series of solvents such as, HCl (1.0 mol L^{-1}), thiourea 3% in HCl (1.0 and 2.0 mol L^{-1}), HNO_3 (2.0 and 3.0 mol L^{-1}) and $Na_2S_2O_3$ (0.1, 0.2, 0.5, 0.7, 1.0 and 1.5 mol L^{-1}), were used in order to find the best eluent for desorption of Au(III) from the sorbent surface. The results are shown in Table 1. It is obvious that the best recovery was achieved when $Na_2S_2O_3$ was used as eluent for the quantitative desorption of Au(III) with concentrations higher than 0.7 mol L^{-1}. Meanwhile, it was also found that the best quantitative recovery of Au(III) was obtained with 6.0 mL of 1.0 mol L^{-1} $Na_2S_2O_3$. Therefore, 6.0 mL of 1.0 mol L^{-1} $Na_2S_2O_3$ was used as the optimum conditions in the subsequent experiments.

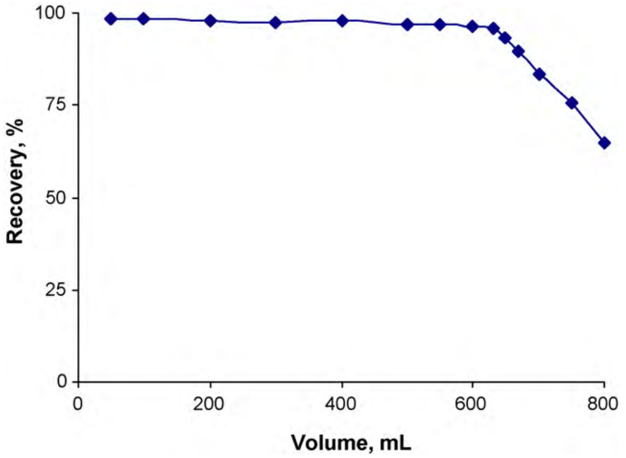

Fig. 3. Breakthrough volume. Conditions and instrumental setting were same as in Fig. 2.

Table 2
Effect of foreign ions (Au(III), 10.0 μg).

Ion	Tolerance limit (mg)
CH_3COO^-	20.0
$H_2PO_4^-$, PO_4^{3-}	50.0
SO_4^{2-}	15.0
Mg^{2+}, Ca^{2+}	150.0
Cu^{2+}	10.0
Cd^{2+}	2.9
Hg^{2+}, Pb^{2+}	0.8
Al^{3+}, Fe^{3+}	7.0
Zn^{2+}, Ni^{2+}, Mn^{2+}	6.0
Rh^{3+}	2.5
Ag^+, Co^{2+}	1.4
Pd^{2+}	1.3

Conditions and instrumental settings were same as in Fig. 2.

3.4. *Breakthrough volume*

In order to explore the possibility of enriching analytes from natural water with a high preconcentration factor, the effect of sample volumes from 50 to 800 mL containing 600 ng of Au(III) was studied at the optimum conditions. The results depicted in Fig. 3 show that Au(III) ions were quantitatively recovered when the sample volume was less than 630 mL. When the sample volume exceeded 630 mL, the recovery decreased. Consequently, by considering the final elution volume of 6.0 mL of $Na_2S_2O_3$ and a breakthrough volume of 630 mL, a preconcentration factor of 105 was easily achievable.

3.5. *Interferences*

Matrix effect is an important problem in the determination of metals in real samples. In order to assess the suitability of the developed procedure in analysing real samples, the interference of several cations and anions was examined under optimized conditions. Various salts and metal ions were added individually to a solution containing 10.0 μg of Au(III) ion, and the procedure was applied. The tolerance limit was set as the concentration of foreign substances required to cause a ±5% error. The results were shown in Table 2, clearly indicate that most of the tested ions do not interfere with preconcentration and determination of gold. Thus, the selectivity of the proposed method is high enough to be used for determination of gold ions in environmental samples.

Table 3
Determination of gold in water samples.

Sample	Added ($ng\,mL^{-1}$)	Found[a] ($ng\,mL^{-1}$)	Recovery (%)
Tap water (Mahan)	0.0	N.D.[b]	–
	5.0	5.06	101.2
Well water (Mahan)	0.0	B.L.R.[c]	–
	5.0	4.83	96.6
River water (Gishigan, Rayen)	0.0	B.L.R.	–
	5.0	5.03 ± 0.08	100.6
Sea water (Caspian)	0.0	N.D.	–
	5.0	4.76	95.2
Out flowing wastewater (Copper factory)	0.0	1.34 ± 0.03	–
	5.0	6.31	99.4

Conditions and instrumental settings were same as Fig. 2.

[a] Mean ± standard deviation ($n = 4$).

[b] N.D.: not detected.

[c] B.L.R: below of linear range.

3.6. *Analytical performance*

An analytical figure of merits was evaluated for the determination of gold according to the developed procedure under the optimized conditions. The calibration curve was found to be linear from 0.45 $ng\,mL^{-1}$ to 10.0 $\mu g\,mL^{-1}$ with a correlation coefficient of 0.9990. The procedure was repeated eight times and the relative standard deviation in the determination of 2.0 $\mu g\,mL^{-1}$ of Au(III) ion was found to be ±2.3%. The limit of detection (LOD) was calculated as three times the standard deviation of the blank signal and was 0. 1 $ng\,mL^{-1}$ ($n = 8$) in original solution.

3.7. *Application of the proposed method*

The proposed method was used for the determination of gold in various water samples from the Kerman region in Iran. The results are given in Table 3.

This method was applied to determination of gold in MA-1b reference gold ore. The results, based on the average of four replicates, are tabulated in Table 4. It is clear that they are in good agreement with the certified values.

Table 4
Analysis of gold in the Canadian Certified Reference Material.

Sample	Composition (% or $\mu g\,g^{-1}$)	Found[a] ($\mu g\,g^{-1}$)	Recovery (%)
MA-1b reference gold ore	Si; 24.5, Al; 6.11, Fe; 4.62, Ca; 4.60, K; 4.45, Mg; 2.56, C; 2.44, Na; 1.49, S; 1.17, Ti; 0.38, Ba; 0.18, P; 0.16, Mn; 0.09%, Cr; 200.0, Pb; 200.0, Rb; 160.0, Zr; 140.0, Cu; 100.0, Zn; 100.0, Bi; 100.0, Ni; 90.0, Mo;80.0, Te; 40.0, Co; 30.0, Y; 20.0, W; 15.0, Sc; 13.0, As; 8.0, Ag, 3.9, Sb; 3.0, Au; 17.0 $\mu g\,g^{-1}$	16.57 ± 0.26	97.47

[a] Mean ± standard deviation ($n = 4$).

Table 5
Comparison of modified nanoclay with other sorbents for preconcentration and determination of gold.

Sorbent	Determination technique	Preconcentration factor	Detection limit ($ng\,mL^{-1}$)	Ref.
Carbon nanotubes	FAAS	75	0.15	[15]
Thiol Cotton Fiber	GFAAS[a]	–	0.02	[16]
Octadecyl Silica Membrane Disks Modified by Pentathia-15-Crown-5	FAAS	100	1.0	[17]
Aminopropyl Silica Gel	FAAS	100	4.12	[18]
Silica Gel/NanoMeter TiO_2	FAAS	50	0.21	[19]
Amberlite XAD-2000	FAAS	200	16.6	[20]
Dowex 4195	FAAS	31	1.61	[21]
Modified organo nanoclay	FAAS	105	0.1	This work

[a] GFAAS: graphite furnace atomic absorption spectrometry.

3.8. *Comparison of modified organo nanoclay with other sorbents*

The present sorbent for preconcentration trace amounts of gold in the aqueous samples compared with other sorbents and the results are shown in Table 5 [15–21]. The proposed sorbent shows a comparatively low detection limit ($0.10\,\mathrm{ng\,mL^{-1}}$) and high preconcentration factor (105) for Au(III) separation. As can be seen, this sorbent has a higher preconcentration factor and a lower detection limit than in other studies [15,17–21].

4. Conclusion

This study demonstrates the suitability of modified organo-nanoclay sorbents for the separation and preconcentration of trace amounts of Au(III). The proposed procedure for the modification of organo nanoclay is simple and, due to the possibility of multiple use of sorbent, is also economical, representing a potentially significant advantage in the preconcentration and analytical separation of gold ions. The method was applied for the determination of gold ions in water samples as well as standard samples and was found fast, precise, accurate and reliable with the preconcentration factor of as high as 105.

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